Development of Stronger and More Reliable Cast Austenitic Stainless Steels (H-Series) Based on Scientific Design Methodology

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Heat-resistant cast austenitic stainless steels are the backbone of the chemical, petrochemical, heat-treating, and metals processing industries

- Tubes for Ethylene cracking, and other chemical processes
- Radiant burner tubes and fixtures for heat-treating furnaces
- Transfer rolls for steel mill furnaces
- Coiler drums for Steckel mills

Principal Issues

- Current H-series alloys have reached their limits in their high temperature strength properties and their upper use temperature

- Additions of alloying elements have been based on production experience. Such additions improve strength but with side effects such as formation of sigma phase or other embrittling phases

Goals of the Project

- Increase the High-Temperature Creep Strength by 50%
- Increase upper Use Temperature by 30 to 60ºC (50 to 100ºF)

Objectives of the project

- To use scientific methodology and computational alloy development tools to modify existing cast heat-resistant austenitic stainless steels
  - Create a favorable microstructure and control the microstructure that develops in specific components during service exposure.

- To develop a computational tool that facilitates alloy selection for specified properties and is based on the knowledge developed from this project

Energy Benefits

Higher operating temperatures will result in more efficient processes

Energy savings: 38 trillion BTU in the year 2020

Assumptions:

- **Chemical Industry: 0.5 % improvement in the ethylene cracking process**
- **Steel Industry: 1.0 % improvement in the heat-treating operations and hot rolling of steel**
- **Heat-Treating Industry: 1.0 % improvement in the efficiency of heat-treatment furnaces**

Economic Benefits

Cost savings of $185 million in 2020 due to:

- **Reduced costs due to energy savings**
- **Better production efficiency**
- **Reduced downtimes**
- **Reduced consumption of components**

Multi-Industry Participants

Primary Participant

Duraloy Technologies Inc.

Users

- Bethlehem Steel Corporation
- Harper International
- IPSCO
- NUCOR Steel Corporation
- The Timken Company

Technology Transfer

Energy Industries of Ohio

National Laboratory

Oak Ridge National Laboratory

Approach to Achieve the Program Goal

- Computational Thermodynamics and Kinetic Modeling to Identify the Phases Present in the Cast Compositions of HK and Modified HP
- Micro-characterization of Phases Present to Verify Predictions
- Design and Cast New Alloys

Approach to Achieve the Program Goal (Continued)

- Conduct Properties and Verify Results
- Casting Trials at Duraloy
- Verify Welding Response of New High-Strength Compositions
- Develop an Alloy Property/Composition Prediction Software Tool for Commercial Applications

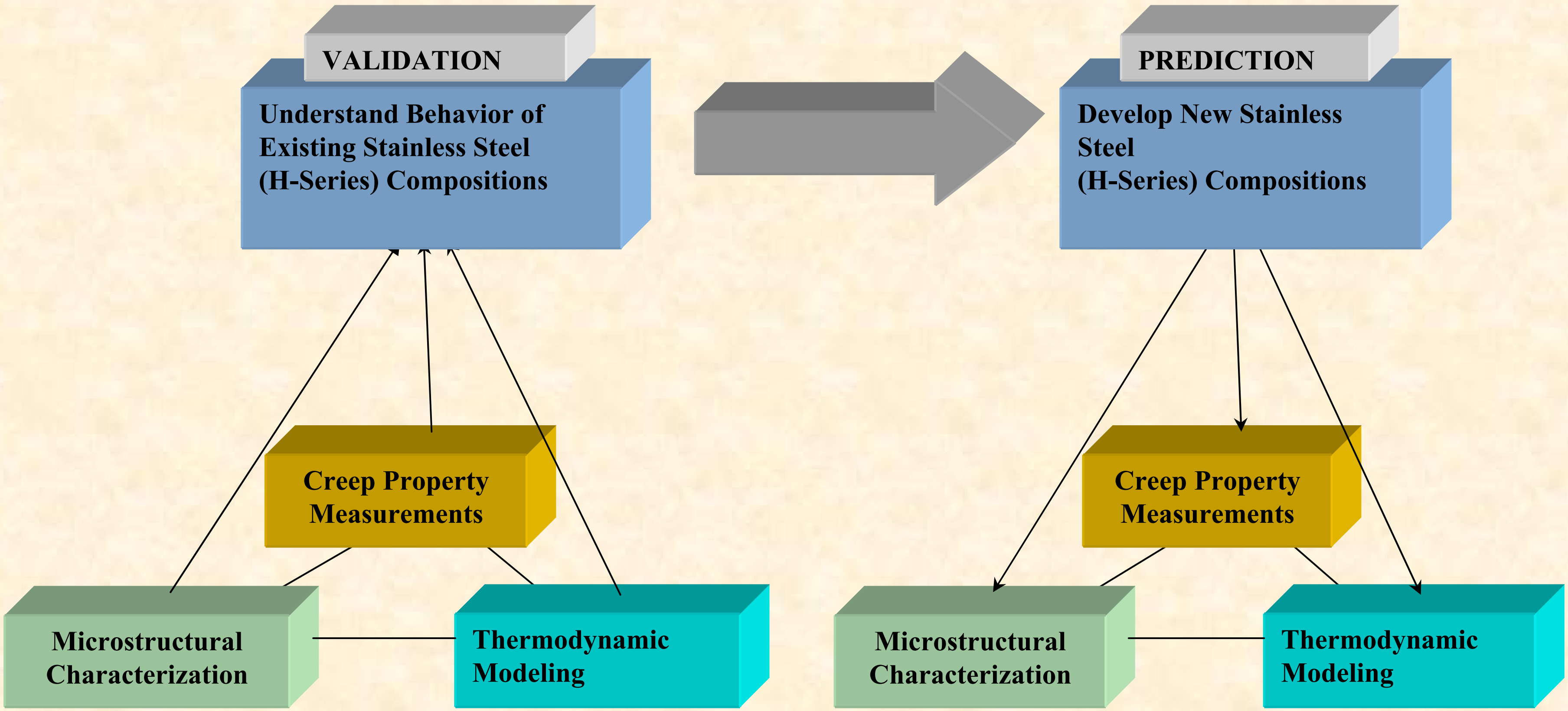
Tasks and Milestones

- Computational thermodynamic analysis of various phases in
  - Existing alloys (Complete)
  - New alloys (on-going)
- Micro-characterization of specimens of existing alloys for verification of computational models and correlation with mechanical properties
  - On-going
- Cast experimental size heats of new compositions
  - On-going
- Determine their mechanical properties
  - On-going

Path to Commercialization

- Develop new alloy compositions and make available to user partners
- Develop new alloy compositions and make available to non-user partners
- Manufactured prototype components will be made available to users for installation in their production systems
- Alloy property/composition predicting software tool for commercial applications will be made available to a broad range of user companies

Overall Technical Approach



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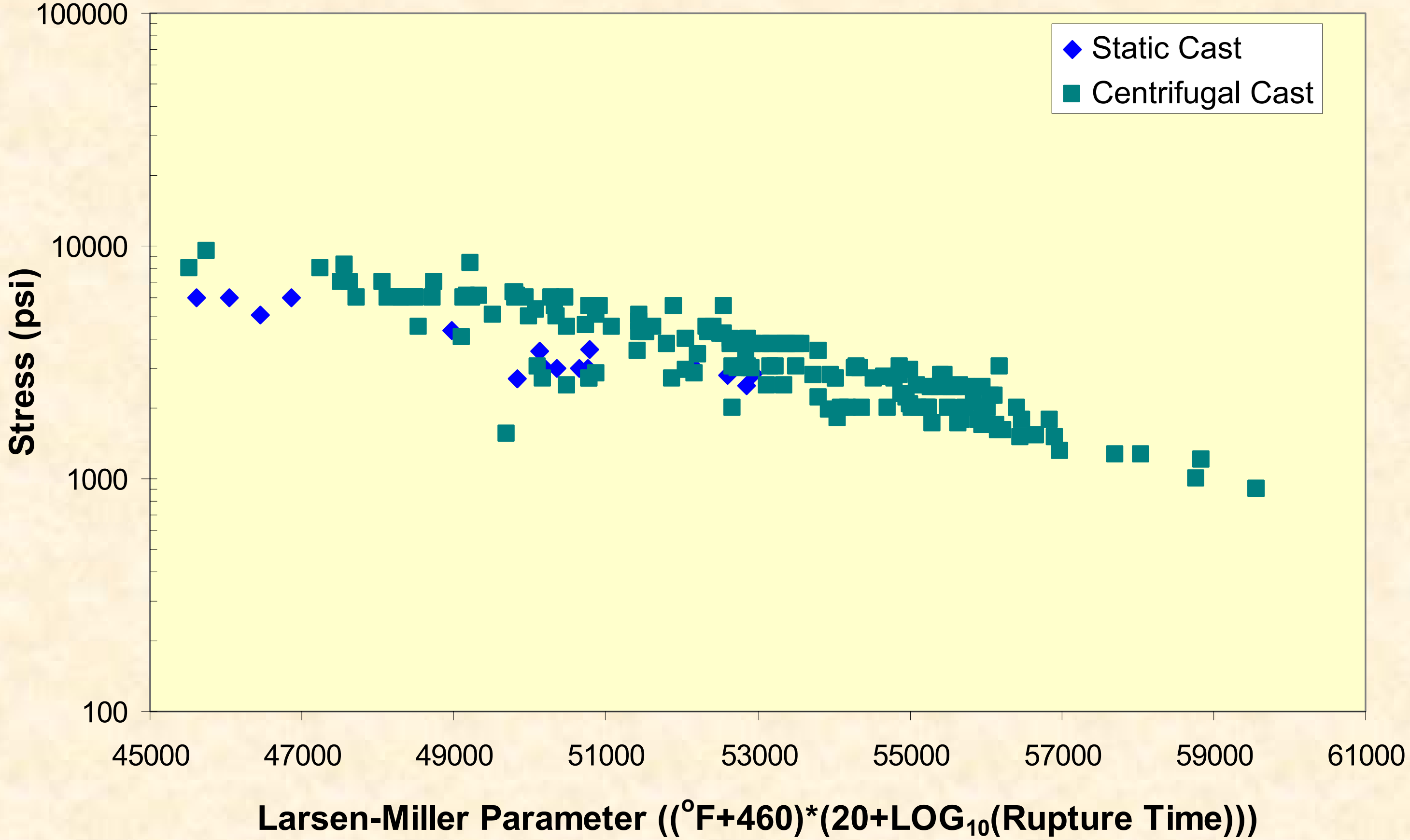
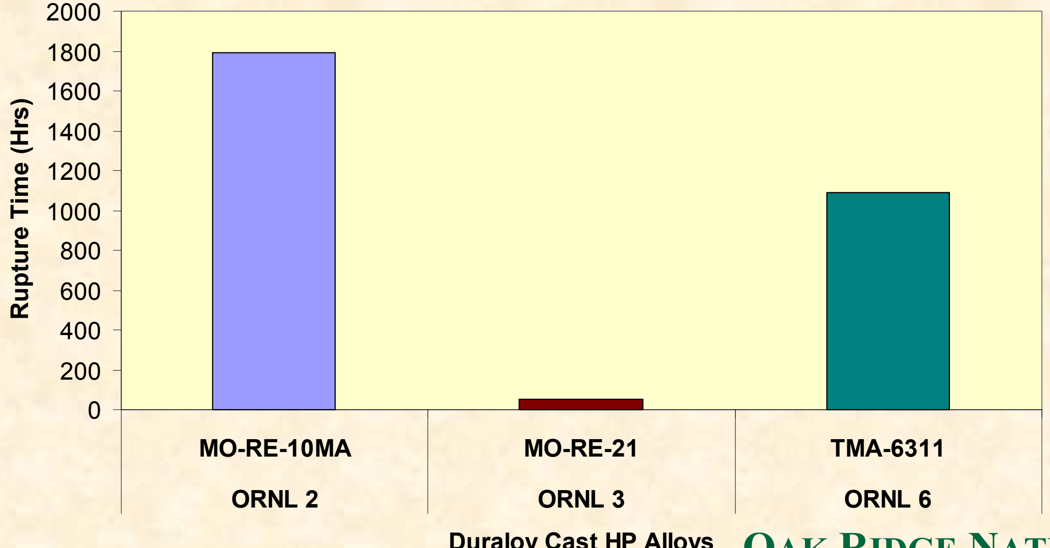
Summary of Creep Data Available on HP-Alloys



ANALYSIS OF DURALOY HP ALLOYS

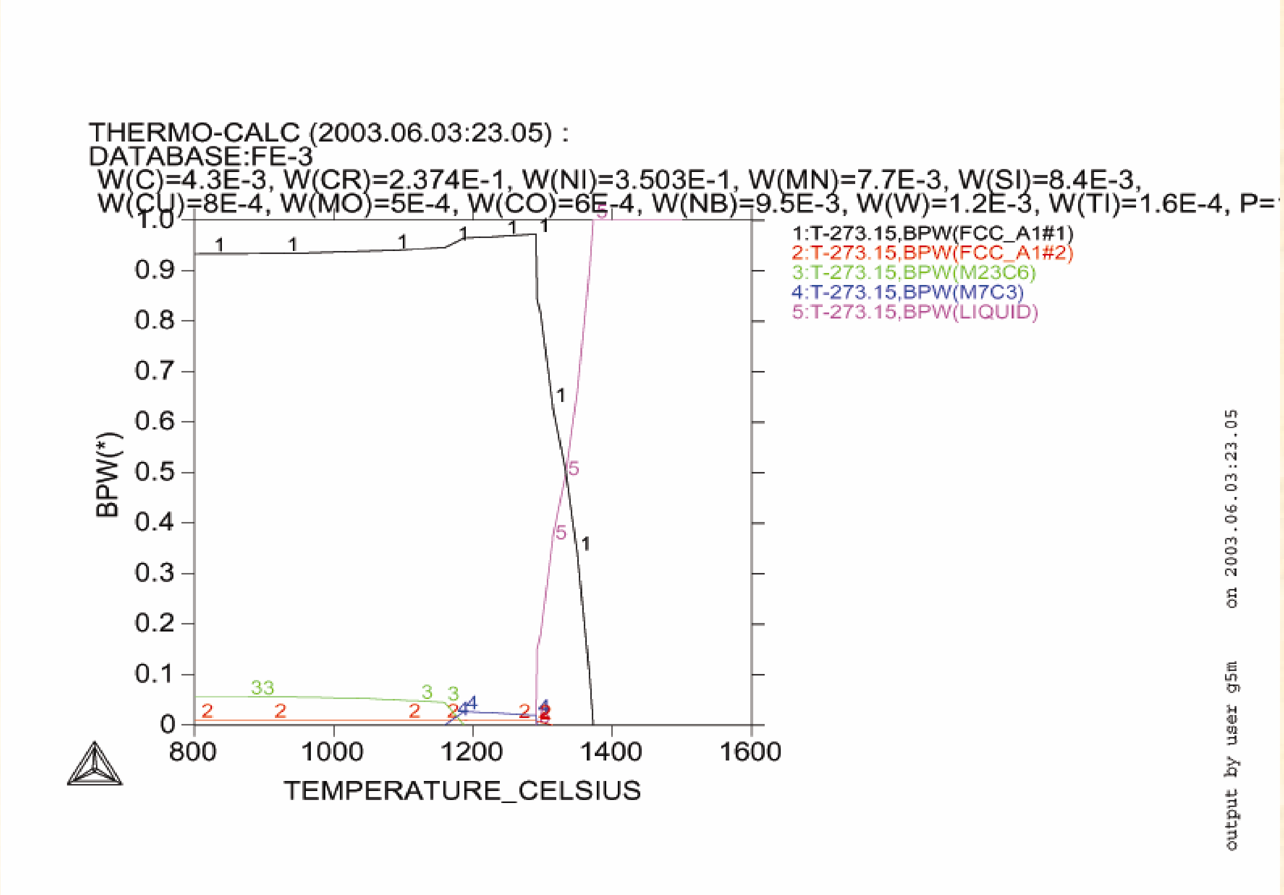
ALLOY	C	Cr	Ni	Mn	Si	Nb	W	Ti	Fe
ORNL 2	0.43	23.74	35.03	0.77	0.84	0.95	0.12	0.016	Bal.
ORNL 3	0.085	20.06	32.37	0.65	0.93	1.22	0.07	0.013	Bal.
ORNL 6	0.42	24.29	32.51	1.31	1.37	0.4	0.33	0.01	Bal.



ThermoCalc^{TM} Modeling of HP Alloys

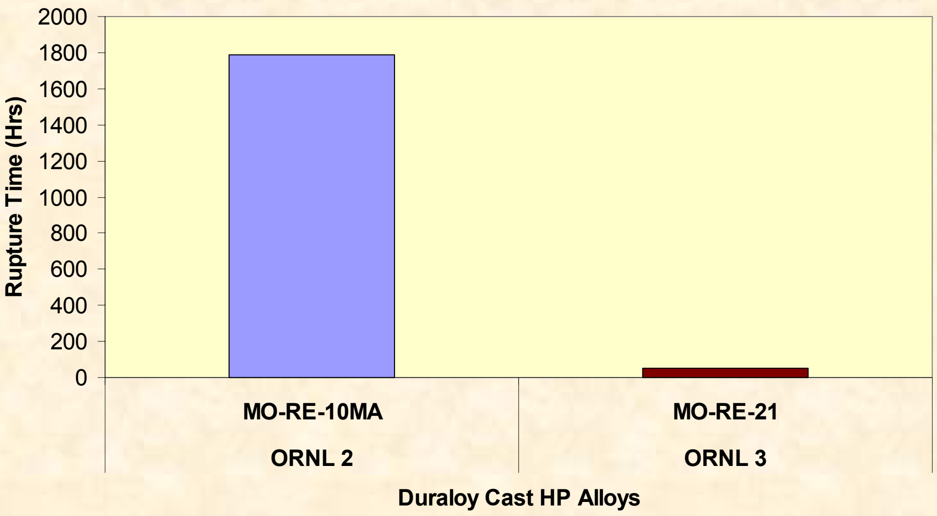
- ThermoCalc^{TM} uses existing information on free energies of various phases in Fe-alloys to predict which phases result in lowest free energy of the system
  - Input to calculations: T, P, Alloying elements present, Phases to be considered in the calculations
  - Output from calculations: Phases present, their compositions, and amounts
- Two types of calculations have been performed:
  - Equilibrium, applicable to slow cooling
  - Non-equilibrium (Scheil) applicable to rapid cooling

Typical Output From ThermoCalc™: Phases Present at Equilibrium as A Function of Temperature in ORNL 2

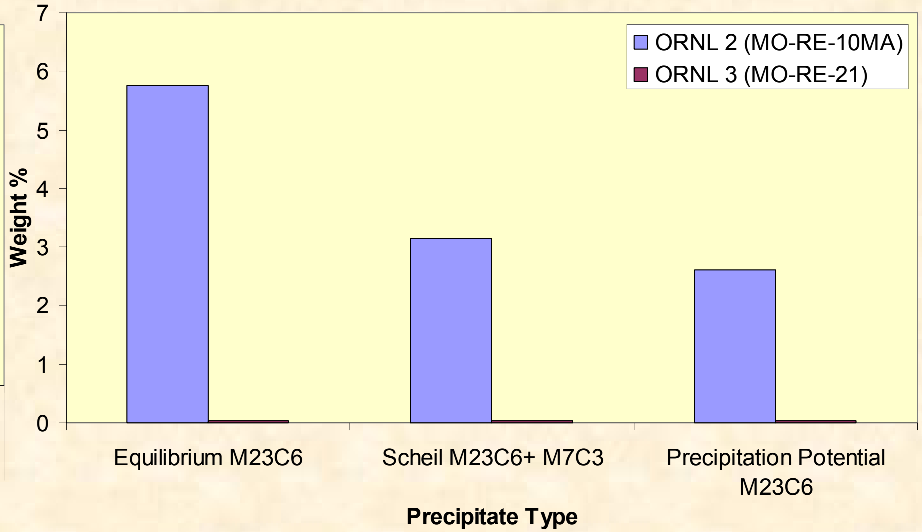


Creep Properties of Duraloy Alloys Correlate well with Relative Amounts of $M_{23}C_6$ Predicted by Modeling

Creep Properties



Calculated $M_{23}C_6$ Contents



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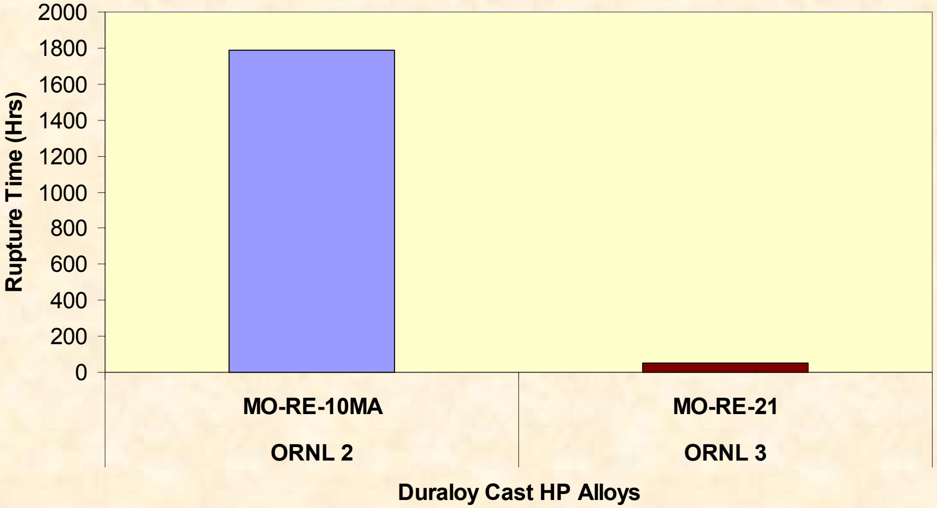
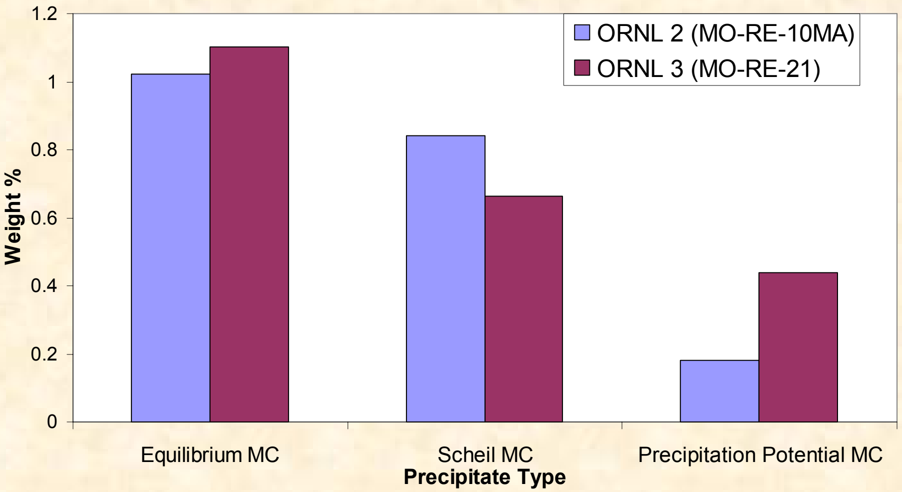
Creep Properties of Duraloy Alloys Show Minimum Correlation to Amounts of MC Predicted by Modeling

Creep Properties



Calculated MC Contents



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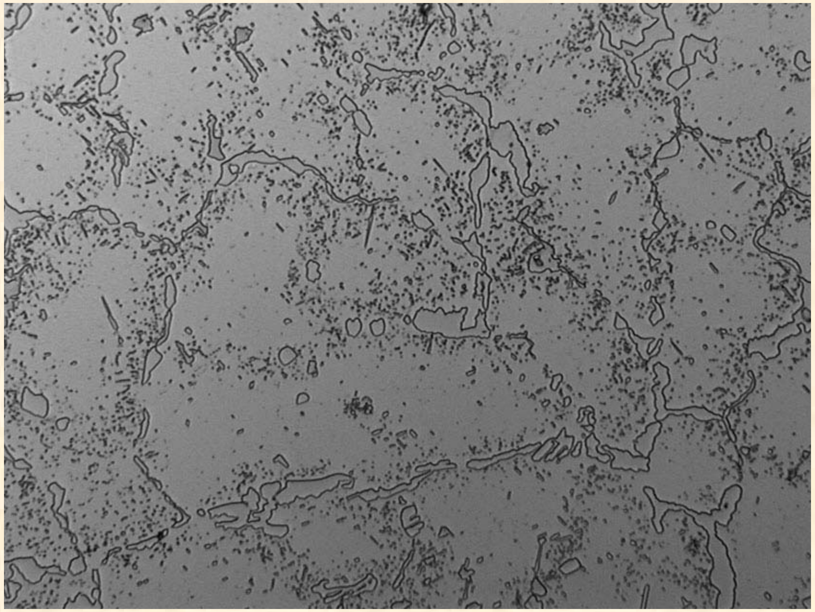
Micro-Characterization of Alloys

Two main purposes

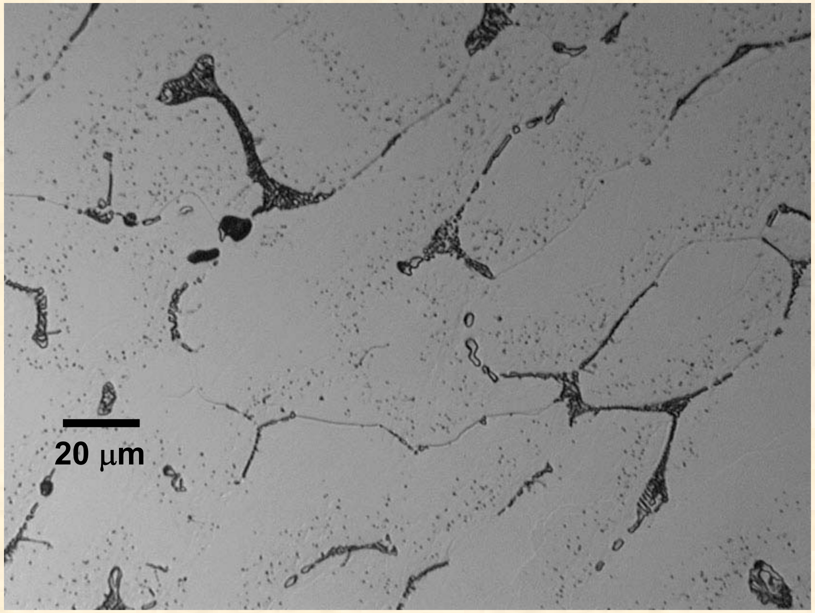
- Test/validate ThermoCalc™ predictions regarding phases present, amounts of phases, and compositions of phases
- Study the sizes (fine vs. coarse) and distribution of phases within the microstructure (grain boundary vs. grain interior)

Optical Microscopy Shows Significantly More Precipitation in the ORNL 2 Which has Better Creep Resistance

ORNL2

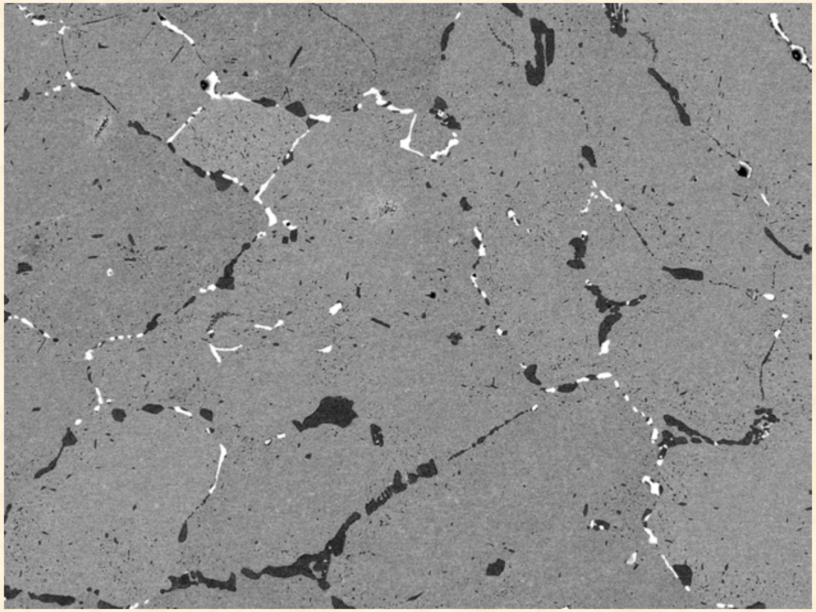


ORNL3

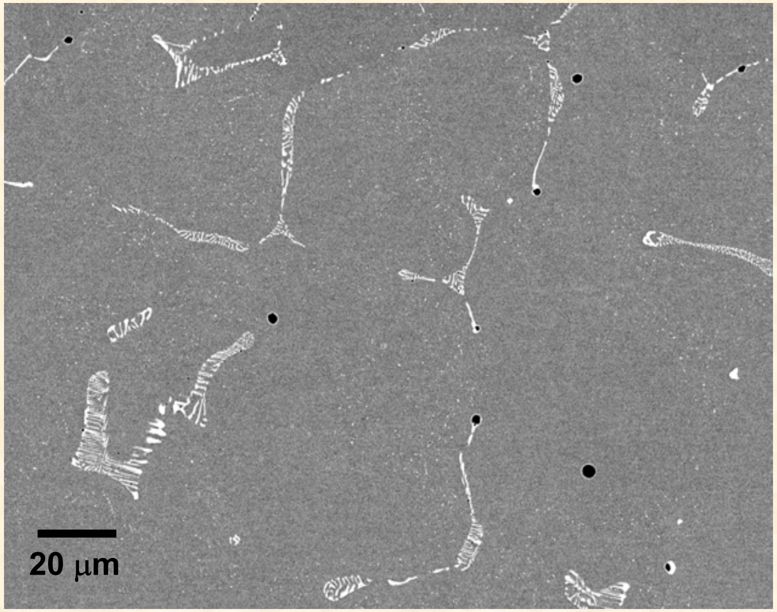


Back-Scattered Scanning Electron Microscopy Shows Differences in the Types of Phases Present in the Two Alloys

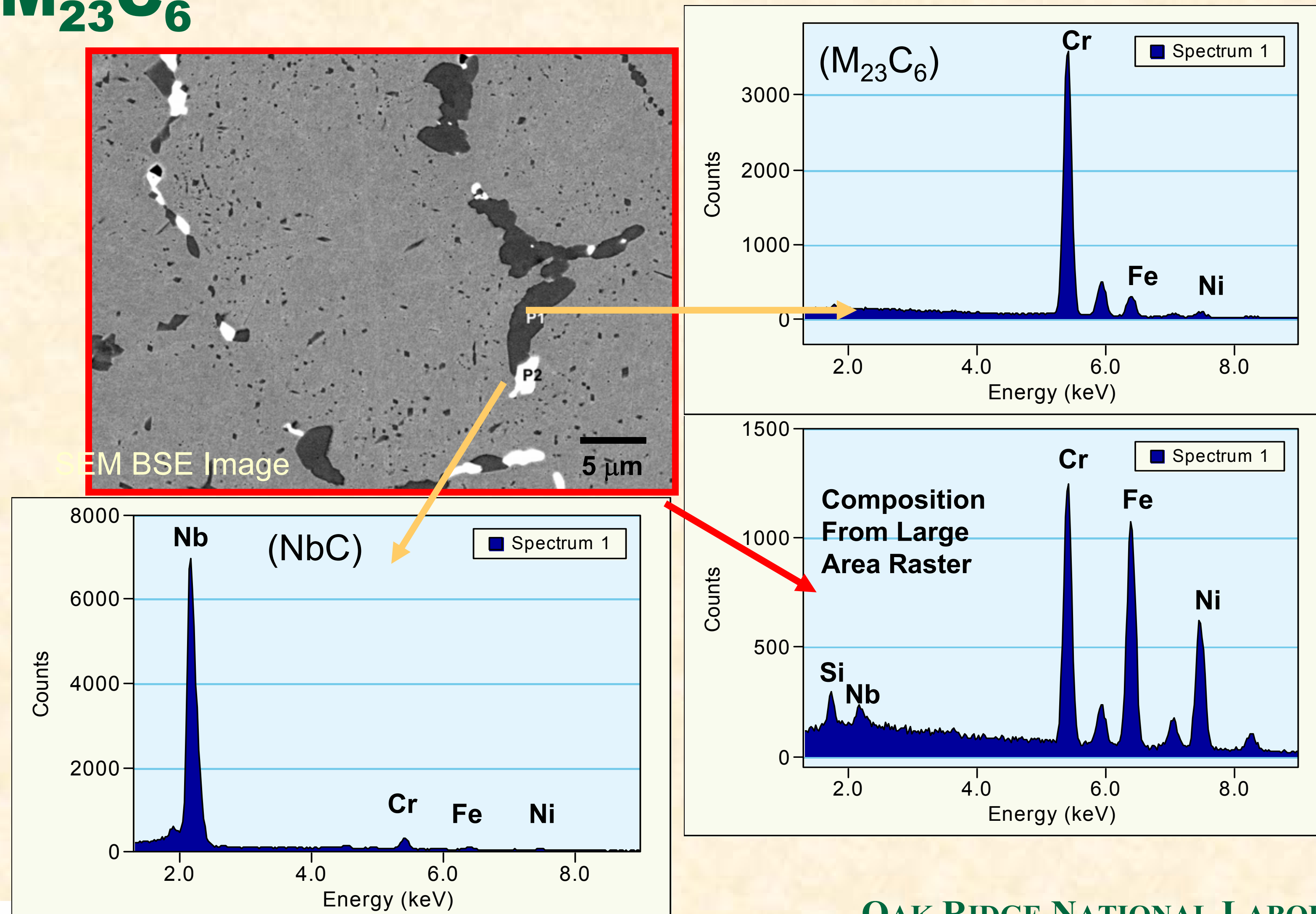
ORNL 2



ORNL 3



Energy-Dispersive X-ray Analysis Reveals that the Interdentric Phases in ORNL2 are NbC and $M_{23}C_6$



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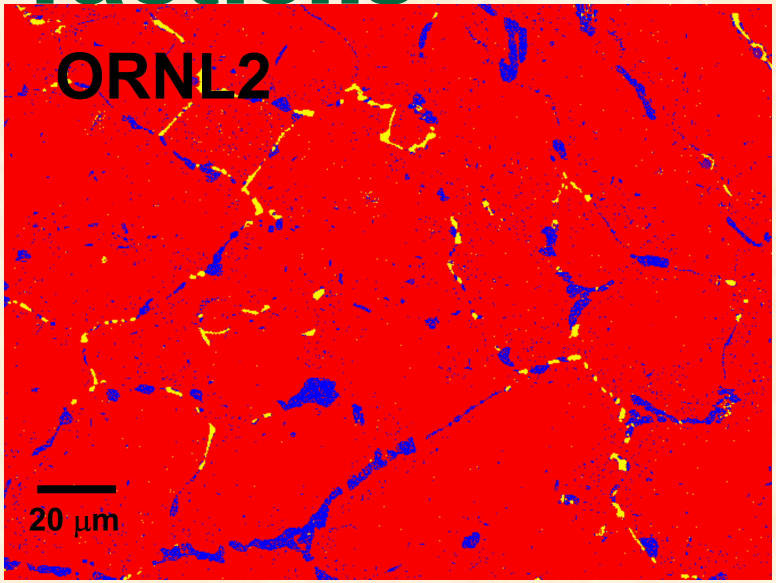
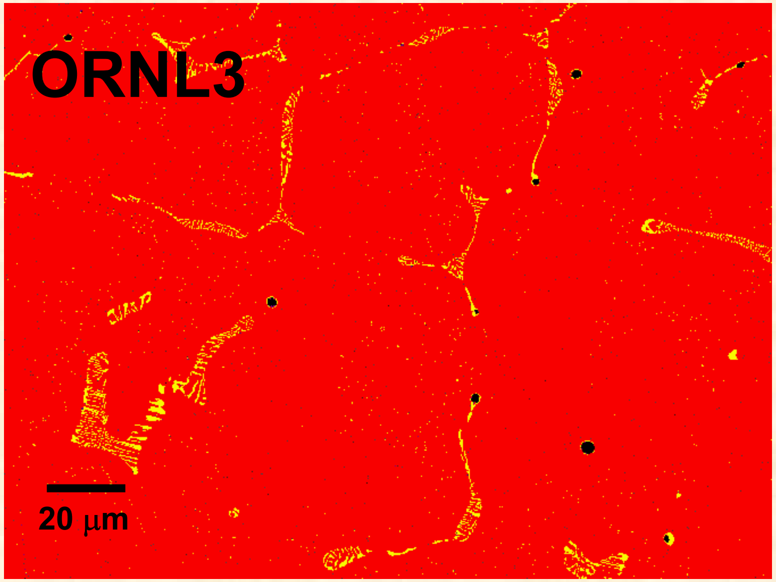
ThermoCalc™ Predictions Compare well with SEM Measurements of Area Fractions



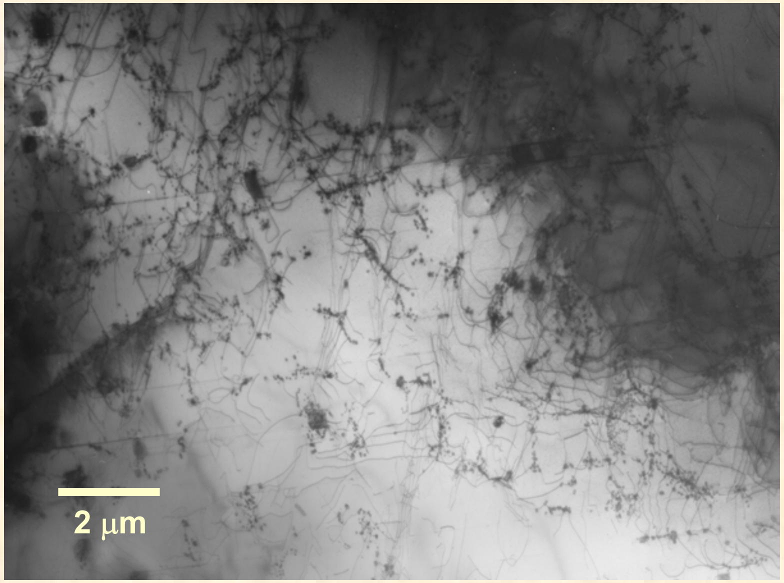


Phase	Color	Meas.	ThermoCalc™ Predictions (Scheil)	ThermoCalc™ Predictions (Equilibrium)
γ		95	95.5	92.42
$M_{23}C_6$		4	3.59	6.49
MC		1	0.91	1.09

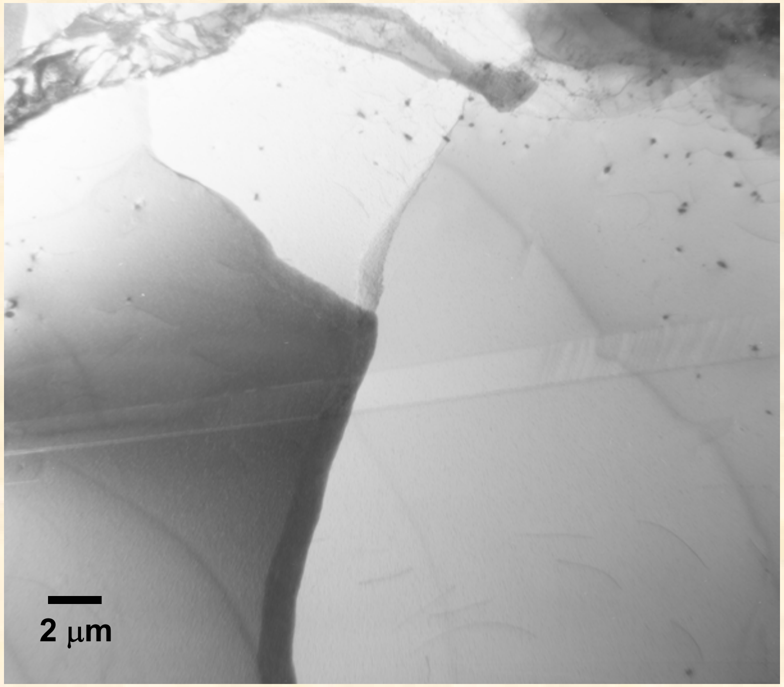
Phase	Color	Meas.	ThermoCalc™ Predictions (Scheil)	ThermoCalc™ Predictions (Equilibrium)
γ		98.3	98.83	98.85
$M_{23}C_6$		0	0	0
MC		1.7	0.65	1.15
Laves		0	0.52	

Transmission Electron Microscopy Shows Significant Precipitation of Fine MC and $M_{23}C_6$ Within The Grains in ORNL 2

ORNL 2



ORNL 3



Objectives for Optimization of Target Microstructure of Alloys

- Promote the formation of fine, stable matrix precipitates while maximizing the strength of austenite

- Promote the formation of stable carbide structures to strengthen the grain boundaries

- Stabilize the austenite against the formation of embrittling phases

- Increase the resistance of the matrix to microstructural failure phenomena

Experimental Alloys Developed And Cast at ORNL

- Two series of alloys: High Si and Low Si

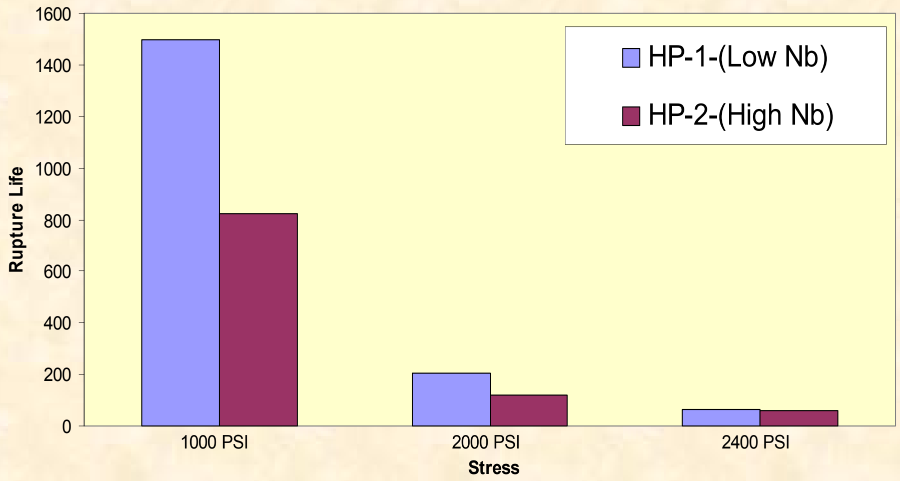
Compositions of High Si Alloys Cast at ORNL

ALLOY	C	Cr	Ni	Mn	Si	Nb	W	X	Y	Fe	Comments
HP-1	0.40	22.69	34.63	0.75	1.46	**1.03**	0.12	0.018	0.002	Bal.	Nominal Nb
HP-2	0.41	22.97	35.16	0.76	1.49	**2.1**	0.13	0.036	0.002	Bal.	High Nb

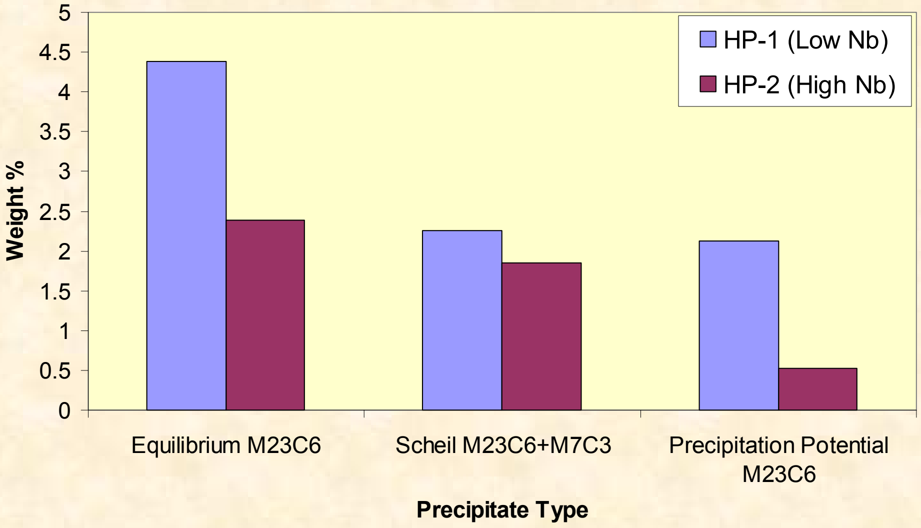
ThermoCalc Modeling™, Mechanical Property Measurements, and Micro-characterization of these alloys are on-going

Rupture Lives at 1093°C as a Function of Stress for High Si Alloys and Correlation with $M_{23}C_6$ Contents

Creep Properties



Calculated $M_{23}C_6$ Contents



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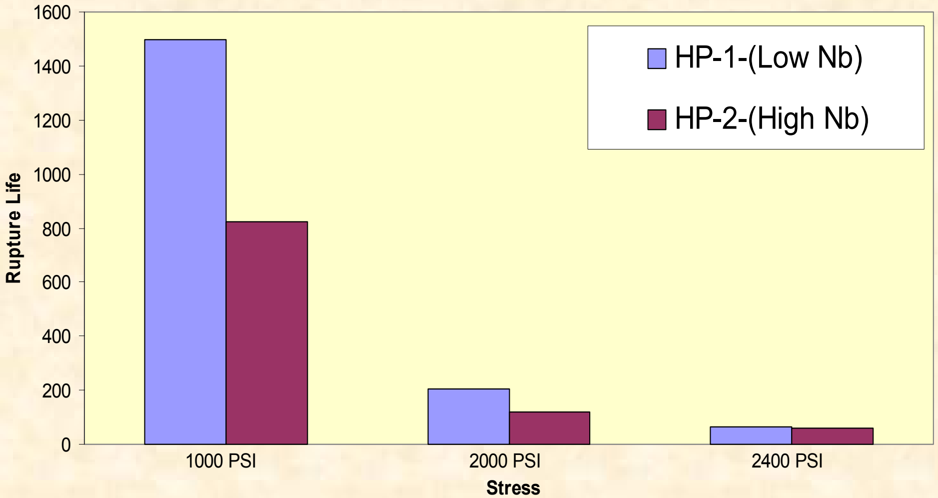
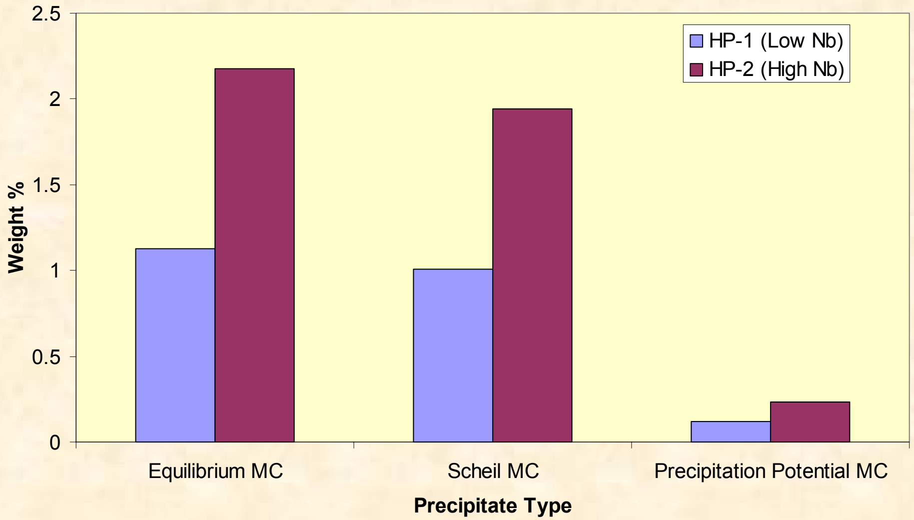
Rupture Lives of High Si Alloys at 1093°C Show Minimal Correlation With MC Contents

Creep Properties



Calculated MC Contents



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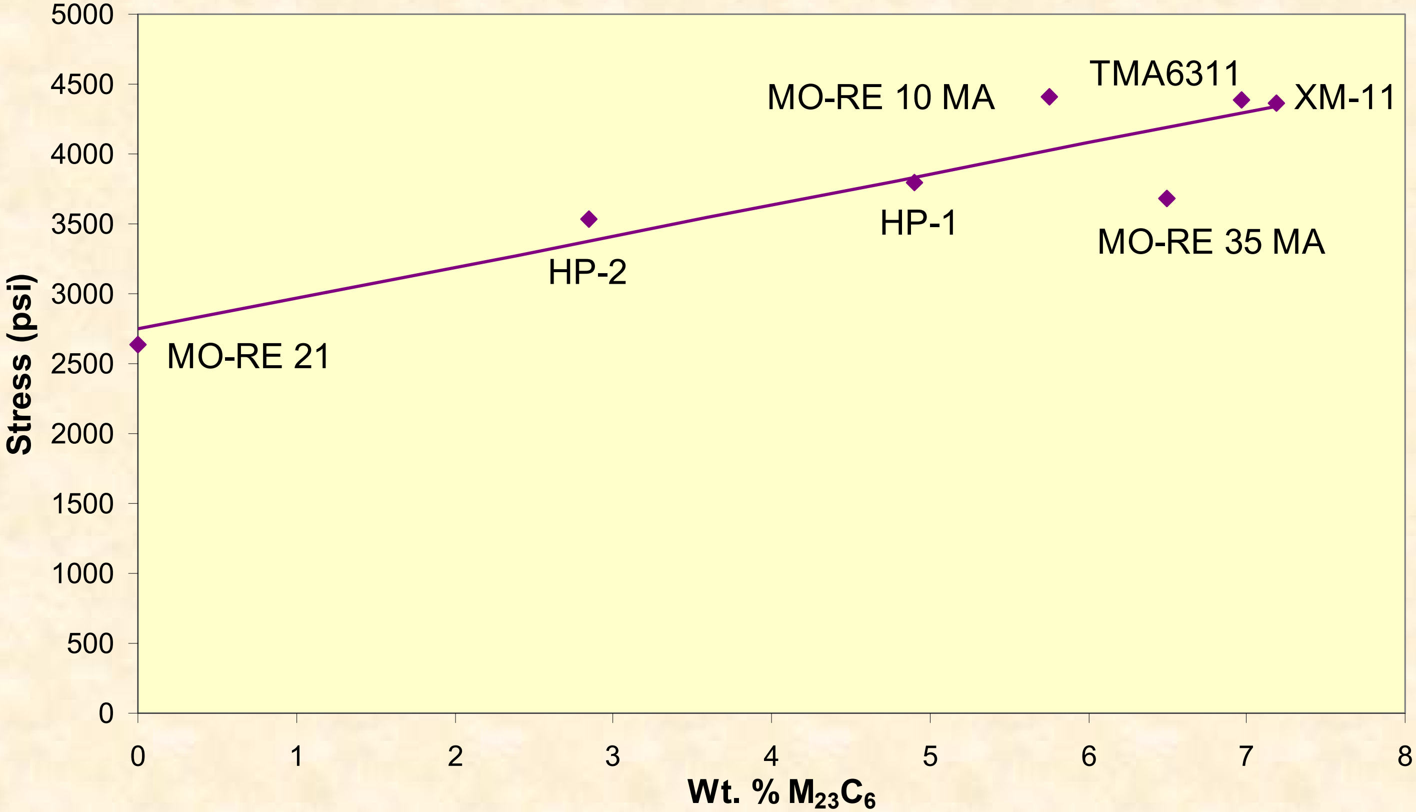
Experimental Alloys with Low Si Contents Cast at ORNL

ALLOY	C	Cr	Ni	Mn	Si	Nb	W	X	Y	Fe	Comments
HP-3	0.38	23.51	34.52	0.97	0.65	1.02	0.08	0.012	0.002	Bal.	Base Alloy
HP-4	0.41	23.49	34.46	0.96	0.65	1.0	**0.32**	0.013	0.002	Bal.	High W
HP-5	0.48	23.63	34.53	1.03	0.66	0.5	0.08	**0.028**	0.002	Bal.	Small X
HP-6	0.42	23.65	34.52	1.01	0.65	0.51	0.08	0.012	**0.02**	Bal.	Medium Y
HP-7	0.41	23.65	34.63	1.04	0.67	0.33	0.08	**0.097**	0.002	Bal.	Medium X

Summary of Results of Creep Tests on Alloys with Low Si

Low-Si Alloy	Steady-State Creep-Rate at 982°C, 4Ksi (Hr^{-1})	Hours to Failure	Comments (All Compositions in wt. %)
HP-3	0.00164	746	1.02Nb, 0.012X, 0.002Y Base alloy
HP-4	0.00145	984	1.0Nb, 0.32W Lower creep rate than base alloy
HP-5	0.00433	650	0.5Nb, 0.028X Higher creep rate than base alloy
HP-6	0.00174	979	0.51Nb, 0.02Y Longer rupture life
HP-7	0.00081	1200 On-going	0.33Nb, 0.097X Lowest Creep Rate

Weight fractions of $M_{23}C_6$ predicted by ThermoCalc™ have been related to stress for 1000 hour rupture at 982°C



- **Creep properties of existing and newly developed HP alloys show clear correlation with $M_{23}C_6$ contents and will guide further alloy development**

Summary of Current Work

- Using micro-characterization, we have established the validity of ThermoCalc™ modeling for these alloys
- A strong dependence of creep properties on $M_{23}C_6$ precipitation has been demonstrated

Future Plans

- Continue to develop new alloys based on correlations learned from the current study

- Verify relationships between the creep properties and microstructure observed in the existing alloys in the newly developed alloys

- Centrifugal cast alloys and verify properties as a first step in the transfer of the new alloy composition to industrial applications